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# Polyamide 6.6 Modified by DBD Plasma Treatment for Anionic Dyeing Processes

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## 1. Introduction

Plasmatic double barrier discharge (DBD) obtained in air at atmospheric conditions is widely used, among other non-thermal plasmatic alternatives, to modify chemical and physical properties of different textile polymers (Morent et al., 2007).

The impacts of DBD on environmental aspects of textile processing rise to get high attention due to important reduction of costs in dyeing by savings in processing times, products, human resources, water and energy (Carneiro et al., 2001). All fibers, from natural to synthetics, can be submitted to several irradiation methods with diverse and significant meaning in different areas of textile processing (Sparavigna, 2001).

The effects on surface are reported for cellulosic fibers (Carneiro et al., 2005; Souto et al., 1996), wool (Rakowski, 1992), polyester (Oktem et al., 2000, Leurox et al., 2009), polyamide 6.6 (Papas et al., 2006; Oliveira et al., 2009), polyamide 6 (Dumitrasku & Borcia, 2006), polytetrafluoroethylene (Liu et al., 2004), polyethylene (Oosterom et al., 2006), polypropylene (Yaman et al., 2009) and meta aramid (Chen et al., 2008), being roughness, microporosity and creation of polarity by oxidation mechanisms the main modifications induced by several types of irradiation techniques.

Acid dyes are the most common in use for polyamide dyeing, but some problems are very well known, as difficulties to manage uniformity and fastness. The necessary pH to achieve a good exhaustion of dye in the fiber must be carefully controlled and sometimes is excessively low.

Reactive dyes are very important for the dyeing of cellulosic and protein fibers, but in polyamide the results are not equivalent due to paler colors obtained (Soleimani et al., 2006). Reactive dyes for cellulose are similar to acid dyes in their chromophoric structure, but they possess reactive groups able to react chemically with the fiber in the presence of alkali. Only few of these dyes have been developed for polyamide application with ability to react with amino groups in fiber structure without the need of alkaline fixation. Stanalan (Dystar) and Eriofast (Ciba) are well known dyes for this purpose.

Reactive dyes for cotton fibers, Procion (Dystar), Kayacelon (Nippon Kayaku), and Drimarene (Clariant) were tested for polyamide dyeing at boiling temperature and different pH showing distinct results. At pH 4, the most convenient result was obtained due to a high protonation of nucleophilic amino groups, contributing to electrostatic attraction between anionic dye and positively charged fiber (Soleimani et al., 2006).

In order to achieve better dyeing results in polyamide fibers some trials are reported in the bibliography using new techniques for structural changes, being irradiation by means of lasers and plasmas presented as promising solution.

Low temperature plasmas via several gases such as oxygen, tetrafluoromethane and ammonia were used for modification of fibers i.e. wool and polyamide 6. Dyeing of modified fibers was performed with several natural dyes and the dyeing rate of the plasma-treated wool was considerably increased (Wakida et al., 1998).

Polyamide 6 was treated with tetrafluoromethane low temperature plasma and then dyed with commercially available acid and disperse dyes. Acid dyeing results show that this type of plasma treatment slows down the rate of exhaustion due to an increase in hydrophobic groups at the surface originated by the type of gas used, without reduction of the amount of dye absorption at equilibrium.

The dyeing properties of disperse dyes on plasma-treated polyamide fabrics markedly increase comparing with untreated fabric by increasing hydrophobic attraction between disperse dye and the fiber (Yip et al., 2002).

Polyamide 6.6 fabric was dyed with a disperse-reactive dyestuff and a covalent bonding with the fiber was proved to occur if supercritical carbon dioxide is used (Liao et al., 2000).

Polyamide 6 materials irradiated with 193 nm ArF excimer laser developed micro-sized ripple-like structures on the surface, able to increase surface area and light diffuse reflection. Laser treatment is proved to be responsible by breaking the long chain molecules of polyamide resulting in an increase of amine end groups' content. Results revealed that dyeing properties of reactive dyes tested on polyamide fabrics improve after this treatment, in what concerns both kinetics and equilibrium phases (Yip et al., 2004).

In the present work, polyamide 6.6 fabrics were treated with different dosages of an atmospheric double barrier discharge obtained in a semi industrial prototype equivalent to an industrial machine installed in a Portuguese textile plant [Pat. PCT/PT 2004/ 000008(2004)]. The structural and chemical modifications of fabrics were further analyzed in terms of X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques. Moreover, the tinctorial behavior (color strength, exhaustion) of the polyamide fabric dyed with different dye classes, namely reactive dyes for wool, reactive dyes for cotton, acid and direct dyes, was studied as well as washing and rubbing fastnesses.

## 2. Experimental part

### 2.1 Materials

#### 2.1.1 Fabric and dyes

A 100% polyamide 6.6 plain weave fabric (105 g.m<sup>-2</sup>) was used as dyeing substrate. The samples were pre-washed with a solution of 1% non-ionic detergent at 30°C for 30 minutes and then rinsed with water for another 15 minutes, before DBD treatment in order to minimize the contamination.

The dyes used were the following:

**Reactive dyes for cotton** - Levafix Red Brilliant E3BA (C.I. Reactive Red 147), Levafix Yellow CA (C.I. Reactive Yellow 26), Remazol Yellow Golden RNL (C.I. Reactive Yellow 27), Procion Crimson H-EXL (C.I. Reactive Red 231), Procion Yellow H-EXL (C.I. Reactive Yellow 138:1) and Remazol Blue Navy RGB (C.I. Reactive Blue 203).

**Reactive dyes for wool** - Realan Blue EHF, Realan Red EHF, Realan Yellow EHF and Lanazol Blue 3G (C.I. Reactive Blue 69).

**Direct dyes** - Sirius Orange 3GDL (C.I. Direct Orange 57), Sirius Scarlet KCF, Sirius Violet RL (C.I. Direct Violet 47) and Sirius Blue KCFN.

**Acid dyes** - Telon Blue MGWL, Telon Red A2FR and Rot M-6BW.  
All of them were kindly supplied by Dystar ®.

**2.2 Plasma treatment**

**2.2.1 DBD plasma machine**

A double barrier discharge was produced in a semi-industrial machine (Softal/University of Minho) functioning with air at normal temperature and pressure, using a system of ceramic electrode and counter electrode with 50 cm effective width, and producing the discharge at high voltage and low frequency.

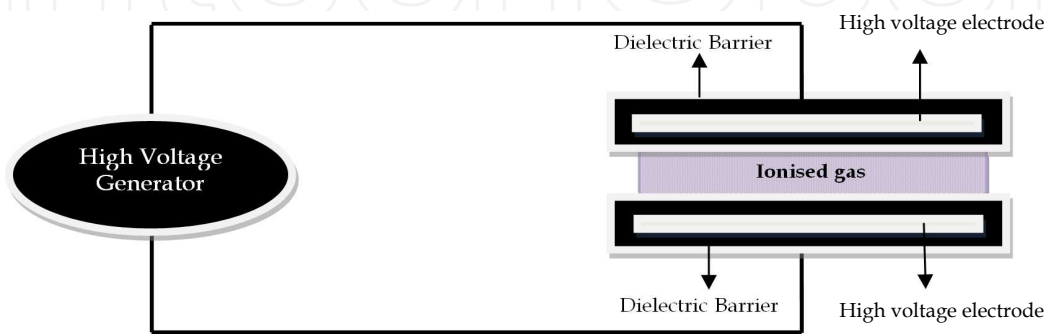


Fig. 1. DBD plasma machine diagram.

**2.2.2 Plasma dosage**

The power of discharge, velocity, number of passages of the fabric between electrodes were variable corresponding to calculated discharge dosages from 400 to 3600 W.min.m<sup>-2</sup> (Table 1). The dosage was calculated according to the following equation (Eq.1):

$$Dosage = \frac{W \times P}{V \times L} \tag{1}$$

Equation 1. Plasma dosage determination, where W = power (Watts); P = number of passages; V = velocity (m.min<sup>-1</sup>) and L = width of treatment (0.5m).

Power (W)	Velocity (m.min <sup>-1</sup> )	Number of passages	Dosage (W.min.m <sup>-2</sup> )
500	2.5	1	400
1000	2.5	1	800
1000	2.5	2	1600
1500	2.5	1	1200
1500	2.5	2	2400
1500	2.5	3	3600

Table 1. Experimental parameters of DBD plasma and dosage applied.

**2.3 Characterization of DBD treated fabrics and structural analysis**

**2.3.1 Water drop absorption test**

In order to evaluate the wettability of the untreated and of the plasmatically modified polyamide woven fabrics, a water-drop test was applied by measuring the time for its complete absorption into the material.

This test is performed in order to check the efficiency of the plasmatic treatment in function of the experimented dosages.

**2.3.2 Contact angle measurement**

Dataphysics equipment using OCA software with video system for the capturing of images in static and dynamic modes was used for the measurement of contact angles of the water drops in polyamide 6.6 fabrics.

**2.3.3 X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy analysis provides information about changes in chemical composition (elemental analysis) and chemical state (wave separation method) of atom types on the fiber surface. The VG Scientific ESCALAB 200A equipment was used to obtain a more detailed and complete analysis.

**2.3.4 Scanning electron microscopy**

Morphological modifications in samples taken from the polyamide 6.6 fabric were analysed with high resolution environmental scanning electronic microscope Schottky FEI Quanta 400FEG / EDAX Genesis X4M. The sample was mounted in aluminum specimen stubs and coated with a layer of gold.

**2.3.5 Atomic force microscopy**

The morphological and topographical characteristics of the polyamide surface before and after DBD plasma treatment were investigated, in a multimode SPM microscope controlled by a Nanoscope III - from Digital Instruments, equipped with an ultra light cantilever with 125 µm long by 30 µm large. The tips were silicon NHC type, with a resonance frequency from 280 to 365 kHz.

**2.4 Dyeing methods**

The dyeing properties were investigated using a dye-bath exhaustion process. The schemes of dyeing processes are shown in figure 2. Various dyeing tests were performed with differents parameters such as temperature, dye concentration (% w/w) and pH, in order to optimise dyeing method and conditions are presented in Table 2. Dyeings were carried out in a laboratorial “Ibelus” machine equipped with infra-red heating and the SIMCORT software was used for continuously assess dye exhaustion from the bath. The samples (each 5.0 g) were dyed with a liquor ratio of 40:1, using stainless steel dyepots with 200 cm<sup>3</sup> capacity each.

Process	Temperature (°C)	Dye concentration (%)	pH
1	100	0.05; 0.1; 1; 2 and 5	4.5 – 5.5
2	100	1	3; 4; 5; 6; 7 and 10
3	90	1	4.5 – 5.5
4	80	1	4.5 – 5.5
5	70	1	4.5 – 5.5
6	60	1	4.5 – 5.5
7	50	1	4.5 – 5.5

Table 2. Parameters used in the dyeing process.

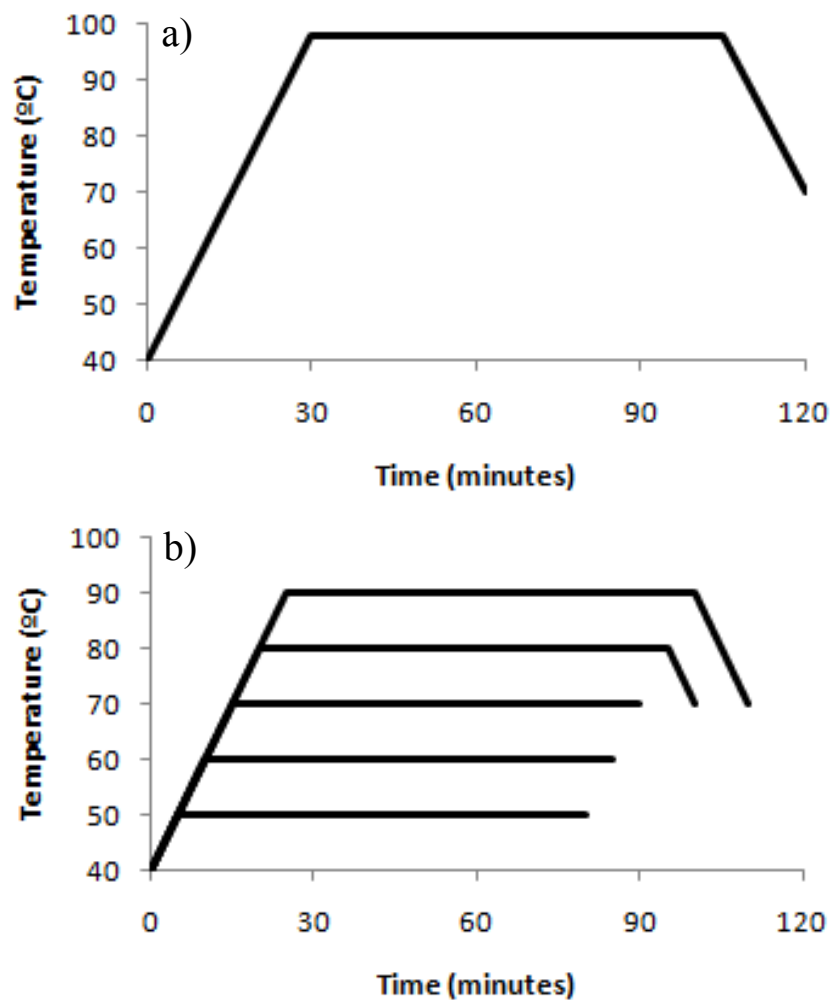


Fig. 2. Dyeing conditions used for (a) Processes 1 and 2 (b) Processes 3 – 7, according with Table 2

2.5 Whiteness and color strength

The whiteness (Berger formulae) of the polyamide fabric after DBD treatment and color intensities of the dyed fabrics were measured by using a Datacolor Spectraflash SF 600 Plus CT spectrophotometer for D65 illuminant, over the range of 390-700 nm. The average of three reflectance measurements, taken at different positions on the dyed fabric, was adopted. The relative color strength (K/S values) was then established according to the Kubelka-Munk equation, where K and S stand for the light absorption and scattering, respectively:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} . \tag{2}$$

2.6 Washing and rubbing fastnesses

The washing fastness was evaluated in accordance with stipulated in standard ISO 105 C06, method A1S, at temperature of 40°C. The rubbing fastness was evaluated according to standard ISO 105 X12:2001.



2.7 Fluorescence microscopy

The level of dye penetration into fibers was visualised by fluorescence microscopy on polyamide transversal cuts. The fibers were embedded into an epoxy resin and transversal cuts of the fibers with 15 mm were prepared using a microtome (Microtome Leitz). Fibers' cross sections were analyzed by a fluorescence microscope LEICA DM 5000B at 40x magnification.

3. Results and discussion

3.1 Optimal plasma dosage

The color depth of dyed polyamide 6.6 was increased by using a reactive dye for wool dyeing (Lanasol Blue 3G), a reactive dye for cotton dyeing (Remazol Yellow Golden RNL) and a direct dye (Sirius Scarlet KCF), when different dosages of plasmatic discharge are used varying power of discharge and number of passages (Figure 3). The K/S values in polyamide samples depend on plasma conditions, being more intense for higher dosages. This criterion was used to choose optimal plasma dosage.

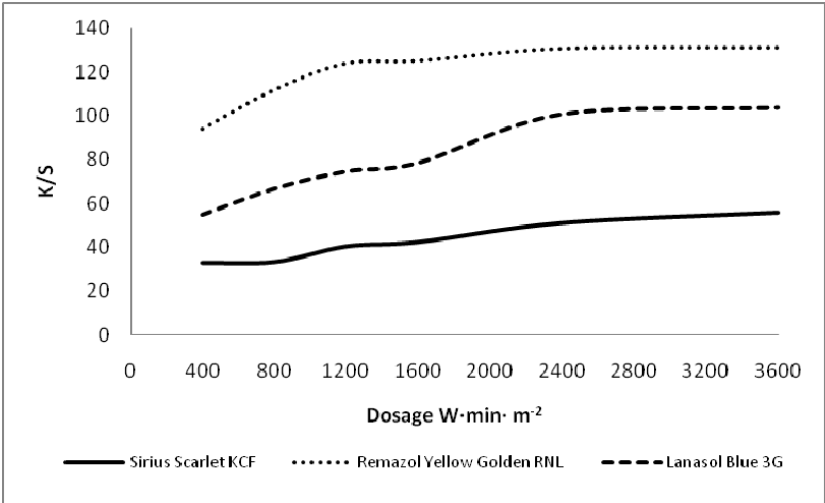


Fig. 3. K/S values of dyed samples of polyamide 6.6 pre-treated with different discharge dosages

A significant difference in the quantity of residual dye is noticed (Figure 4) by comparing colors of the baths obtained after dyeing process of the samples submitted to different dosages.

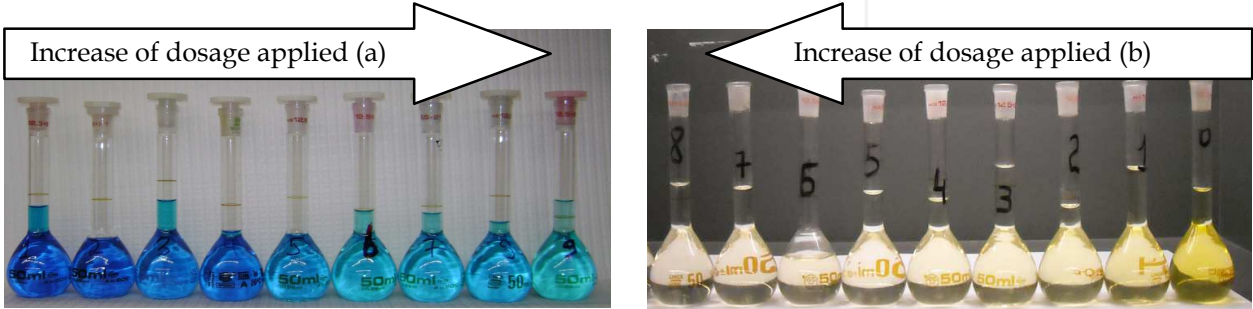


Fig. 4. Final dyeing baths corresponding to samples with increasing dosages of plasmatic discharge – a) Reactive Lanasol Blue and b) Reactive Remazol Yellow Golden.

According to the results obtained, the dosage of 2400 W.min.m<sup>-2</sup> is enough to obtain maximum values of K/S and minimum quantity of dye in residual bath for the three dyes, with the following working parameters in DBD machine: power of discharge -1500 W; speed - 2,5 m.min<sup>-1</sup>; n° of passages – 2. This dosage was further applied to all polyamide samples submitted to dyeing.

3.2 Characterization of DBD treated fabrics and structural analysis

3.2.1 Time of water drop absorption

Table 3 shows the difference between the wettability of the untreated and the plasmatically modified polyamide woven fabrics by measuring the time for complete water absorption into the material.

Tests	Polyamide untreated	Polyamide with DBD treatment
	Time (s)	
01	286.2	56.7
02	293.4	49.5
03	287.5	51.3
04	323.5	50.4
05	323.6	53.6
Mean Values	302.8	52.3
Standard Deviation	19.0	2.9
CV(%)	6.3	5.5

Table 3. Wettability results

3.2.2 Contact angle measurement

The hydrophilicity of the polyamide fabric is highly improved by the plasmatic treatment in accordance with the results published by several authors for different synthetic and natural fibers, mentioning modifications in accessible polar groups at the surface and creation of microporosity (Pappas et al., 2006, Oliveira et al., 2009, Yip et al., 2002). This surface modification might transform the synthetic fiber from hydrophobic to hydrophilic which is key point for the absorption of aqueous dye solutions. The static and dynamic contact angle evaluation of a water droplet in the textile polyamide fabric is shown in figures 5, 6 and 7, corresponding to a mean value of five measurements.

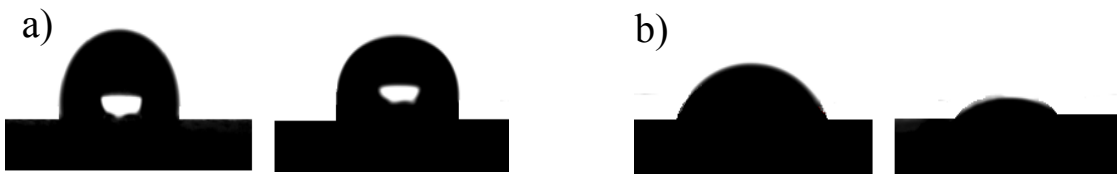


Fig. 5. Contact of water drop in the sample without (a) and with DBD plasma treatment (b) (time =0 s and after 30 s).



After DBD treatment, the wettability of the polyamide fabric considerably increases. This result may be attributed to the incorporation of polar groups onto the fabric surface.

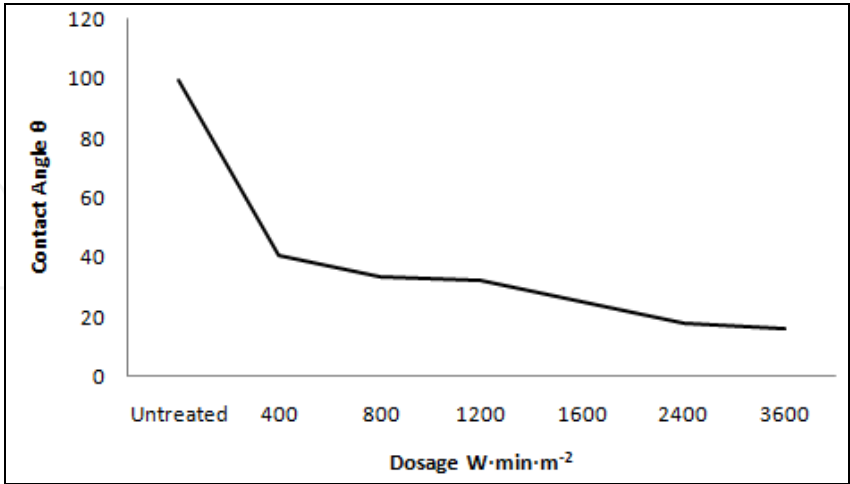


Fig. 6. Static contact angle measurement of a water drop for the samples: untreated and with different plasma dosages.

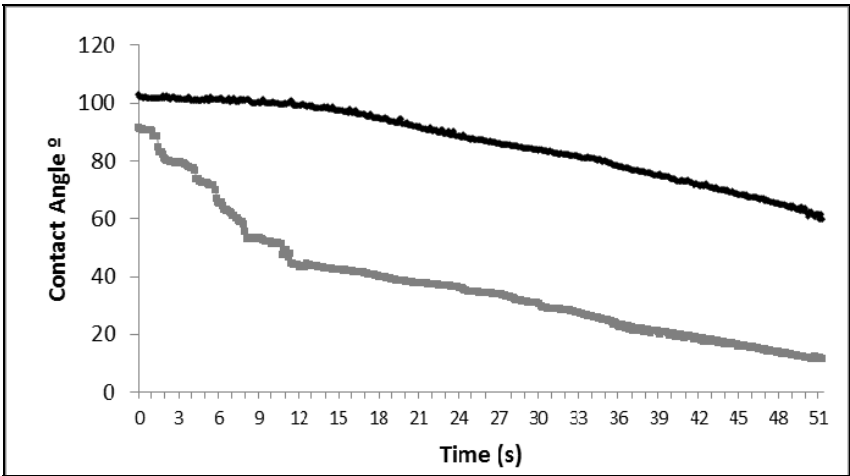


Fig. 7. Dynamic contact angle measurement of a water drop in the sample without treatment (a) and treated with dosage 2400 W.min.m<sup>-2</sup> (b).

3.2.3 X-ray photoelectron spectroscopy

The XPS analysis shows that the oxygen and nitrogen content level was increased after DBD treatment. This indicates a substantial incorporation of these atoms onto the fabric surface. Chemical states of atoms, represented by relative peak areas, can be obtained by wave separation method. The carbon component can be divided into peaks (280.5 to 294.0 eV), assigned as CH<sub>2</sub>, CH<sub>2</sub>CO, CH<sub>2</sub>NH and NHCO (Pappas et al., 2002). It can be observed that the relative peak areas of sub-components change significantly after DBD treatment. Results reveal that the element C1s decreases while both N1s and O1s increase. DBD treatment can be responsible for the breaking of the long chain molecules of polyamide 6.6, causing an increase of carboxyl and amine end groups. The table 4 shows the elementary composition and the atomic ratio before and after plasma treatment.

Sample	Atomic composition (%)			Atomic ratio	
	C	O	N	C/N	C/O
Untreated	74.67	17.75	7.58	9.85	4.21
DBD Treated	70.25	19.83	9.92	7.08	3.54

Table 4. XPS results in samples with and without DBD treatment

The figure 8 shows the increase of O<sub>1s</sub> and N<sub>1s</sub> atoms and consequently decrease of C<sub>1s</sub> when DBD treatment is applied, which corresponds to an enhancement of hydrophilicity of fabrics due to an increase of polar groups in the surface of polyamide fabrics.

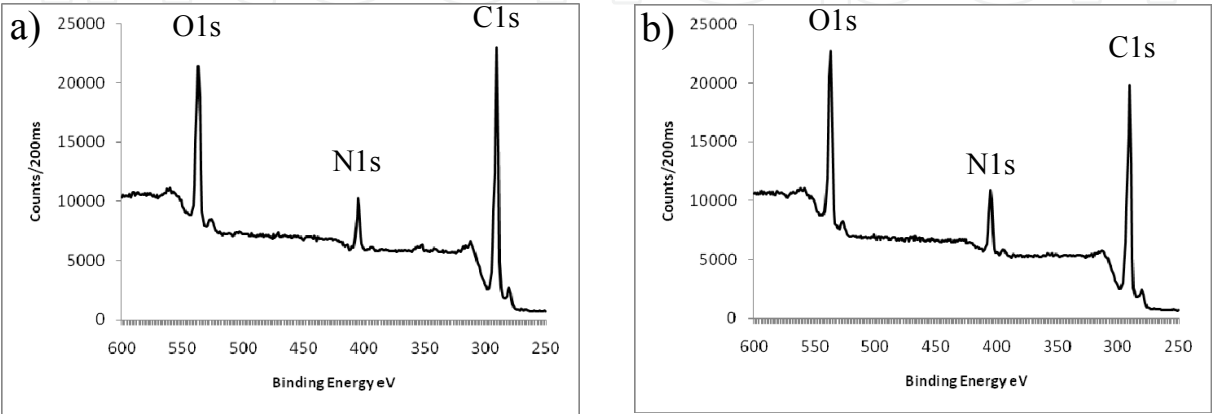


Fig. 8. XPS analysis of polyamide fabric a) without treatment and b) with DBD treatment.

3.2.4 Scanning electron microscopy

The surface modification by DBD plasma on polyamide fabrics was detected by the scanning electron micrographs (Figure 9). Compared to untreated polyamide 6.6, the DBD plasma treated polyamide 6.6 presents small patches on the surface responsible for an increase of surface area. The comparison of the images obtained with and without DBD plasma treatment, shows a somewhat different surface morphology.

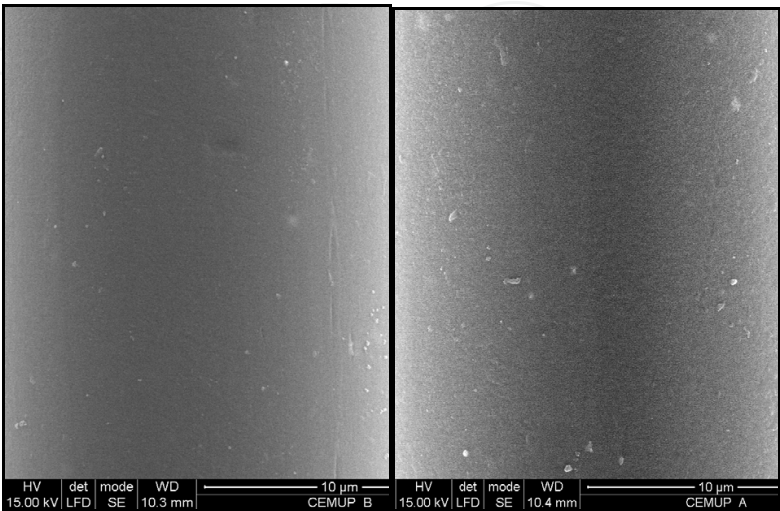


Fig. 9. Increase of roughness after DBD treatment (right) in SEM micrographic

3.2.5 Atomic force microscopy

The increase in roughness can be better understood when AFM images are compared (Figure 10). The following results were obtained for Ra (arithmetic average roughness ), Rq (root mean squared roughness) and Rmax (Table 5), regarding untreated and plasma treated samples.

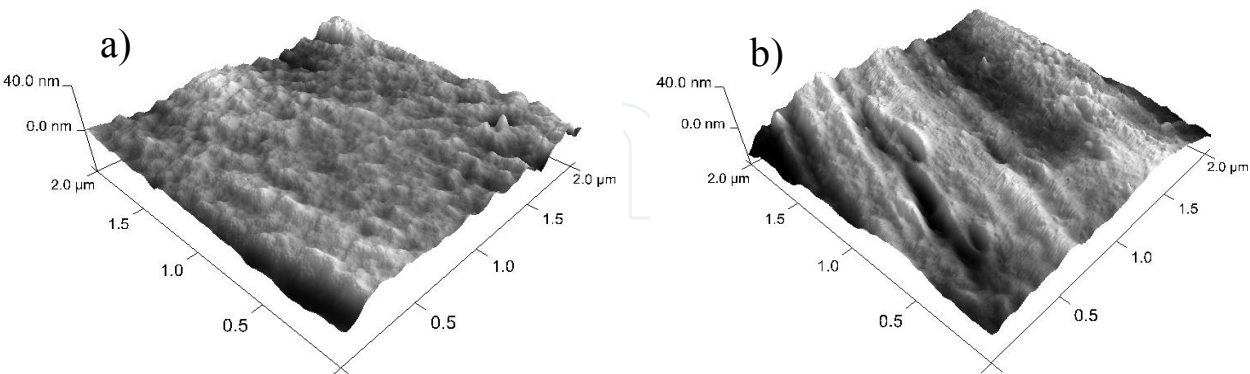


Fig. 10. AFM increase of roughness after DBD treatment (b)

Samples	Ra (nm)	Rq (nm)	Rmax (nm)
Untreated	2.36	3.21	29.2
Treated	6.50	7.99	48.0

Table 5. AFM results for samples with and without treatment

The surface of the sample without treatment is relatively smooth while the treated polyamide has rougher surfaces. The AFM analysis shows that the Ra, Rq and Rmax roughness increases with the DBD plasma treatment and the modification of the shape of surface features is quite evident. The applications of these results illustrate, for example, the increasing of wettability (as showed by contact angle measurements) and consequently polyamide dyeability properties.

3.3 Berger whiteness

The figure 11 shows the results obtained for Berger whiteness when different plasma dosages were applied to the polyamide fabric.

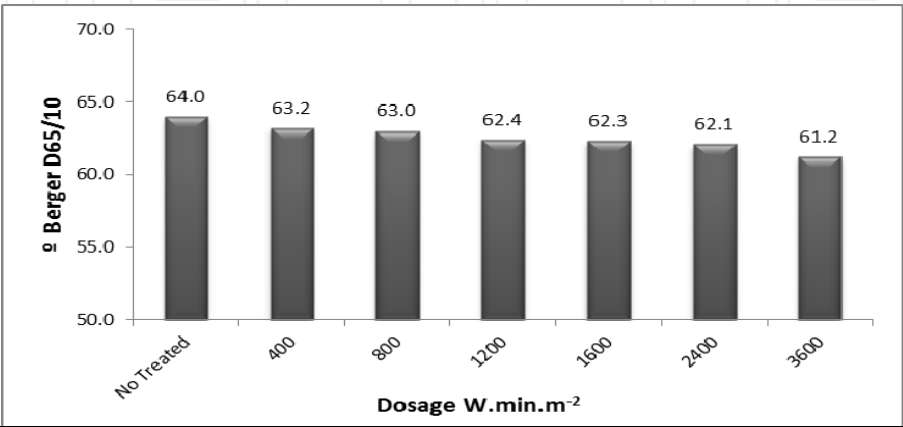


Fig. 11. Whiteness degree – Illuminant D65/observer 10°

Whiteness of polyamide fabric slightly decreases (2.8 degrees for a dosage of 3600 W.min.m<sup>-2</sup>) for higher dosages, although without noticeable effect in product characteristics.

3.4 Dyeing properties

Results show the effect of the plasma discharge on dyeing behavior of polyamide 6.6 with direct dyes, reactive dyes for cotton and wool and acid dyes.

The surface modification of the polyamide fiber after DBD plasma treatment permits very intense and fast colors with dye exhaustion almost reaching 100% in every case.

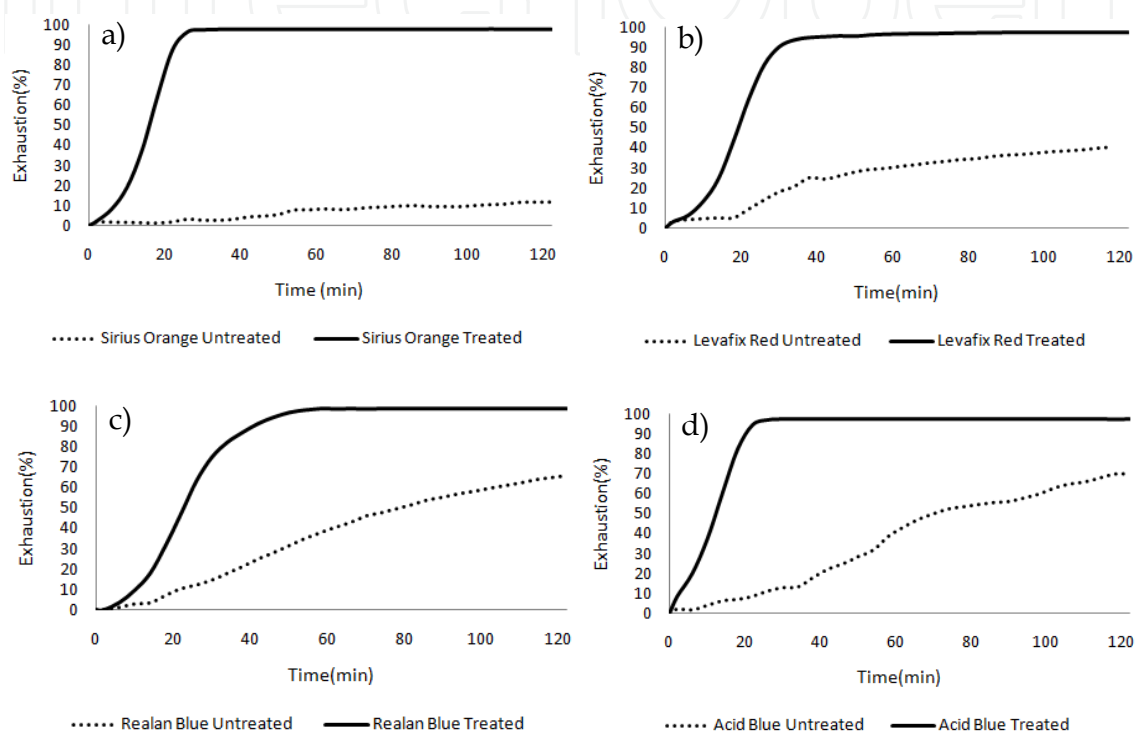


Fig. 12. Exhaustion results for a) direct dye, b) reactive dye for cotton, c) reactive dye for wool and d) acid dye in polyamide 6.6 samples with and without DBD treatment (dyeing conditions: 100°C and 1% dye concentration).

The complete bath exhaustion was obtained in very short time during dyeing processes with remarkable positive difference when a plasmatic treatment is made on polyamide fabrics (Figure 12). Forty minutes are enough to exhaust dye from dyebath which is a very attractive behavior regarding industrial application.

The direct and acid dyes are anionic and water soluble and the increase of fiber hydrophilicity with plasmatic treatment is favorable to dye adsorption, essential to promote coulombic dye fixation to protonated amine groups of the polyamide.

Reactive dyes are also water soluble and anionic, apart being able to form covalent bonding with reactive groups in the fiber, namely the amine groups of polyamide. The same factors promoting adsorption and diffusion of dye in the fiber for the acid dyes are present for reactive dyes, explaining complete exhaustion of dye in the fiber after forty minutes of dyeing.

The table 6 shows the comparative results of K/S with reactive dyes, direct dyes and acid dyes in polyamide 6.6 with and without plasma (DBD) treatment. The results demonstrate

that in dyeings carried with these anionic dyes, the color strength (K/S) is considerably higher for the fabric with DBD treatment, quantified by means of the percentage gain of the treated sample when compared to the non treated one.

Dye Class	Commercial Name	Without Treatment (K/S)	With Treatment (K/S)	DBD gain (%)
Reactive for Cotton	Remazol Golden Yellow RNL	84.4	88.9	5.4
	Procion Crimson H-EXL	15.6	24.9	60.0
	Levafix Yellow CA	43.1	102.6	137.8
Reactive for Wool	Realan Red EHF	36.1	48.6	34.7
	Realan Yellow EHF	54.8	60.9	11.1
	Realan Blue EHF	49.9	86.8	73.9
Direct	Sirius Scarlet KCF	111.6	185.5	137.8
	Sirius Violet RL	100.8	138.7	16.8
	Sirius Orange 3GDL	68.4	199.3	45.8
Acid	Telon Blue MGWL	51.5	66.1	28.3
	Telon Red A2FR	80.7	95.9	18.9
	Telon Rot M-6BW	131.2	149.3	13.8

Table 6. K/S values for dyeings of polyamide 6.6 fabric with and without DBD treatment

The gain in color yield obtained with DBD treatment is effective for all the dyes, although results are quite variable for the different colors of each commercial dye.

3.4.1 The influence of temperature in dyeing processes

The figure 13 shows the influence of the temperature in polyamide dyeing process with the following dyes: Levafix Brilliant Red E-BA (reactive dye for cotton), Sirius Orange 3GDL (direct dye,) Realan Blue EHF (reactive dye for wool) and Telon Blue M-GLW (acid dye). Comparisons were made between the samples with and without plasmatic treatment.

The increase in temperature of all dyeing processes (Figure 13) leads to an increase of the color yield (K/S values) of the polyamide dyed samples. Nevertheless, it is evident that dye absorption mechanism is quite influenced by plasmatic treatment.

In fact, a linear behavior of K/S with temperature is much more present when the fiber is plasma discharged, demonstrating that structural transitions are not the main driving force for dye penetration in polyamide.

Meanwhile it is quite clear that the untreated fiber is highly dependent on temperature to achieve high K/S values, being noticeable that structural changes may occur at temperature around 90°C.

Therefore, the reduction in energy demand can be considerable in the dyeing process when plasmatic pre treatment is made compromising the same color yield (K/S) at much lower temperatures.

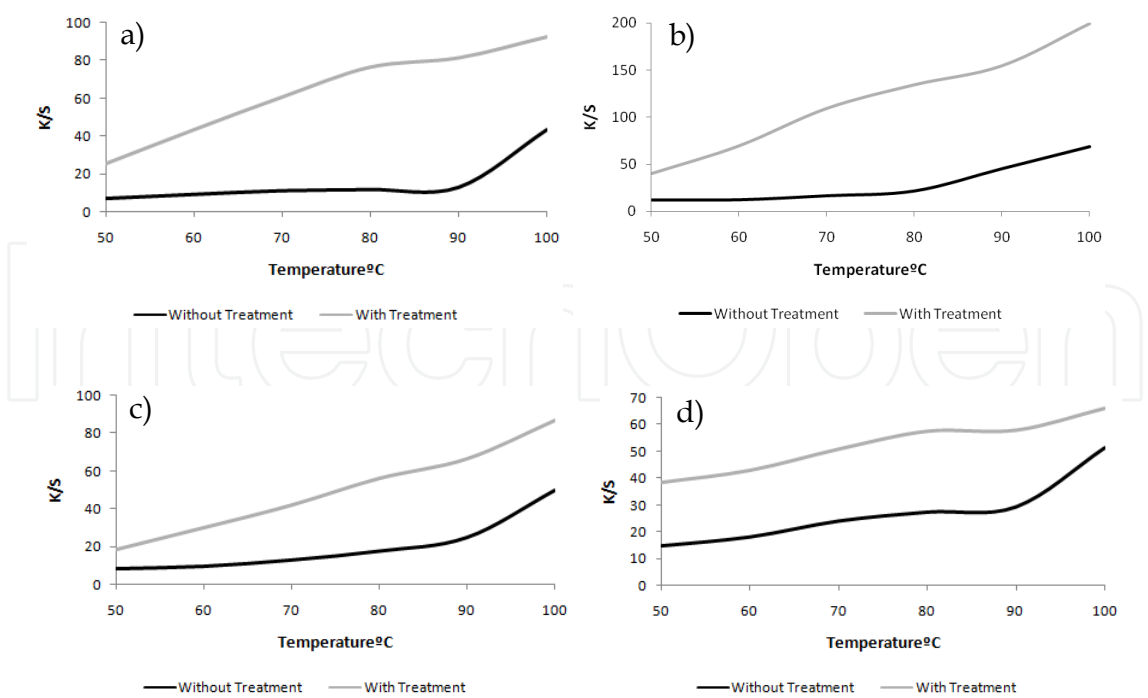


Fig. 13. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different temperatures (dye concentration: 1 % dye weight/fiber weight ).

3.4.2 The influence of dye concentration in dyeing processes

The figure 14 a, b, c and d shows the influence of the dye concentration in the polyamide dyeing.

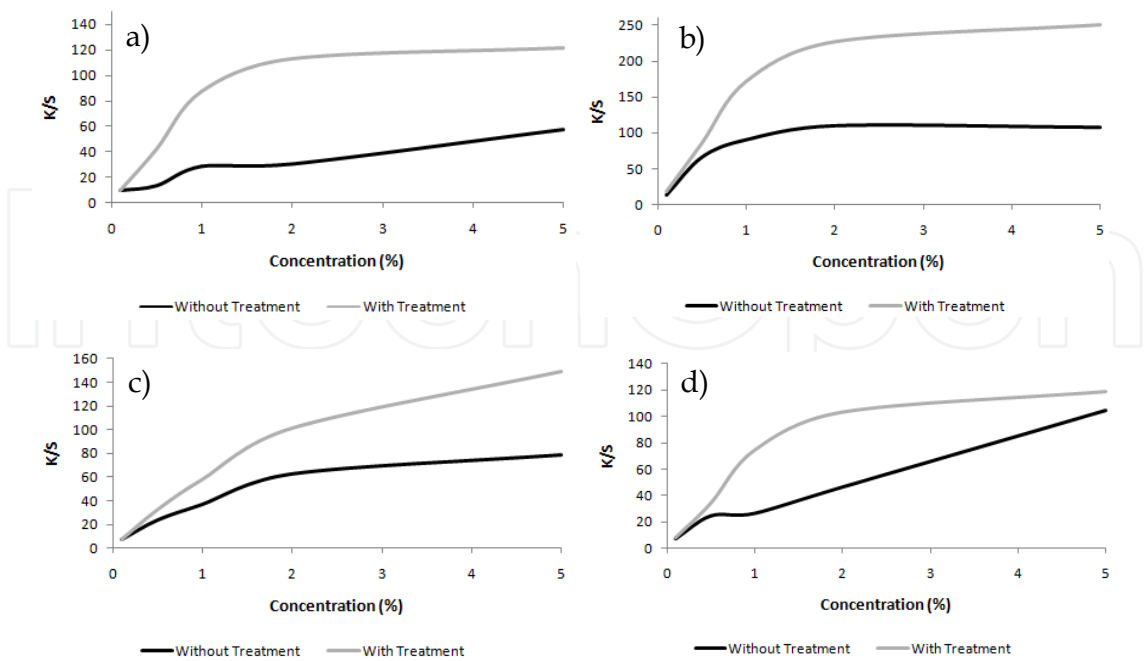


Fig. 14. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different dye concentrations (dyeing temperature: 100°C).



Since polyamide has only a small number of amine end-groups, saturation is easily got and it is difficult to achieve darker colors by dyeing with anionic dyes (Yip et al., 2002; Perkins, 1996).

Figure 14 shows a considerable increase of color yield with the increase of dye concentration being that the total amount of dye in the fiber is always higher after DBD treatment.

Darker colors in the fabric of polyamide 6.6 can be achieved when the plasmatic treatment is applied, with less dye concentration, meaning that is now possible to dye polyamide materials in darker colors by adopting a much more economic process.

The form of the curves concerning polyamide dyeing with the reactive dye for cotton, direct dye and acid dye shows a much higher but limited saturation in plasma treated fabric, whenever the behavior of the reactive dye for wool demonstrates the formation of higher level of linkage groups in the plasmatically treated polyamide.

### 3.4.3 The influence of pH in dyeing processes

The figure 15 a, b, c and d shows the influence of the pH in the polyamide dyeing process, comparing results between the samples with and without plasmatic treatment.

When acid is added to dye bath, the polyamide fiber develops an overall positive charge ( $-\text{NH}_3^+$ ). Thus, in acidic conditions the polyamide fiber becomes positively charged and strongly attracts the negative groups of the anionic dyes. At pH 3 all the studied dyes give similar dyeing yield, either plasma treated or not treated polyamide. However, at pH 3 the polyamide 6.6 fabrics can be degraded, which is very inconvenient for the final quality of dyed materials (Burkinshaw, 1995).

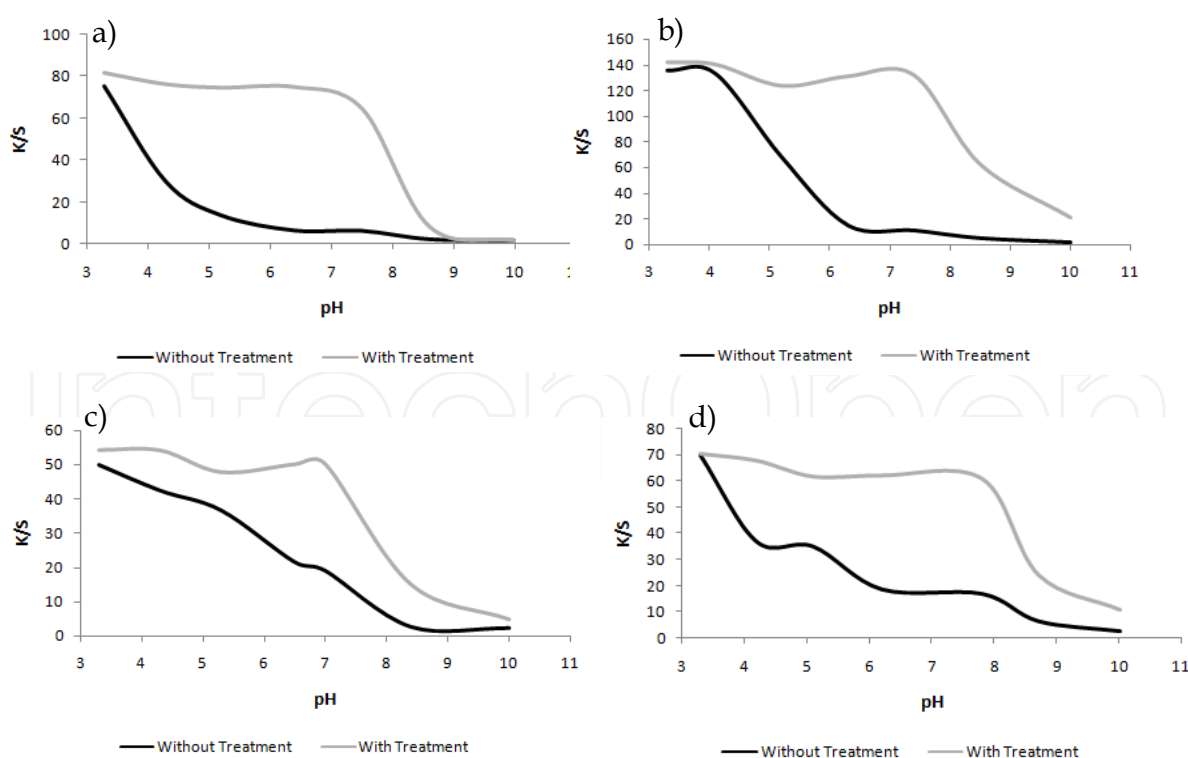


Fig. 15. K/S values of reactive dye for cotton (a), direct dye (b), reactive dye for wool (c) and acid dye (d) in polyamide 6.6 with different dyebath pH (dyeing conditions: 100°C and 1% dye concentration).

When pH of the dye bath is increased, the color yield reduces considerably in the samples without DBD treatment. On the other hand, if samples are treated with plasma and dyed, a type of “buffer systems” can be observed for all the dyeings, propitiating a very important stabilization during the dyeing process in case of pH variations.

Dyeing results are pH independent in the interval 3 to 7, which gives strong indications about the huge influence of plasmatic discharge in chemical composition of fiber surface.

3.5 Washing and rubbing fastnesses

Table 7 shows the results of washing fastness for reactive (wool, cotton) and acid dyes in dyeing of polyamide 6.6.

The results of washing fastness at 40 °C are very good confirming the level of dye diffusion and fixation into the fiber. The surface modification of the polyamide fiber after DBD plasma treatment permits to obtain very fast colors, with the best result for washing fastness.

The results of rubbing fastness in dyed fabrics with and without treatment are very good. The value 5 in the gray scale was obtained for all the samples.

Dyes	Sample	AC	CO	PA	PES	PAC	WO	Color Change
Procion Yellow H-EXL	UT*	4/5	4	5	5	5	4/5	4
	T**	5	4/5	5	5	5	5	4/5
Remazol Blue Navy RGB	UT*	5	5	5	5	5	5	5
	T**	5	5	5	5	5	5	4/5
Levafix Red EBA	UT*	4/5	3	4/5	5	5	5	4
	T**	4/5	3/4	4/5	5	5	5	4
Sirius Orange 3GDL	UT*	5	4/5	5	5	5	5	4
	T**	5	4	5	5	5	5	3
Sirius Blue KCFN	UT*	5	4/5	5	5	5	5	5
	T**	5	4/5	5	5	5	5	4/5
Telon Blue M-GLW	UT*	5	5	5	5	5	5	4/5
	T**	5	5	5	5	5	5	4/5
Realan Blue EHF	UT*	5	4/5	5	5	5	5	4
	T**	5	5	5	5	5	5	4

\*UT - Sample Untreated \*\* T - Sample with treatment

Table 7. Washing fastness of reactive and acid dyeing with previous DBD treatment by Norm ISO 105C06/A1S

3.6 Fluorescence microscopy

Figure 16 shows the results obtained from fluorescence microscopy analysis in the case of polyamide dyed with reactive dyes for cotton (Levafix Red - EBA). The dye shows a perypherical distribution in the sample without treatment (c), while in the case of the plasma treated sample the dye presents a deeper diffusion into the core of the fiber (d).

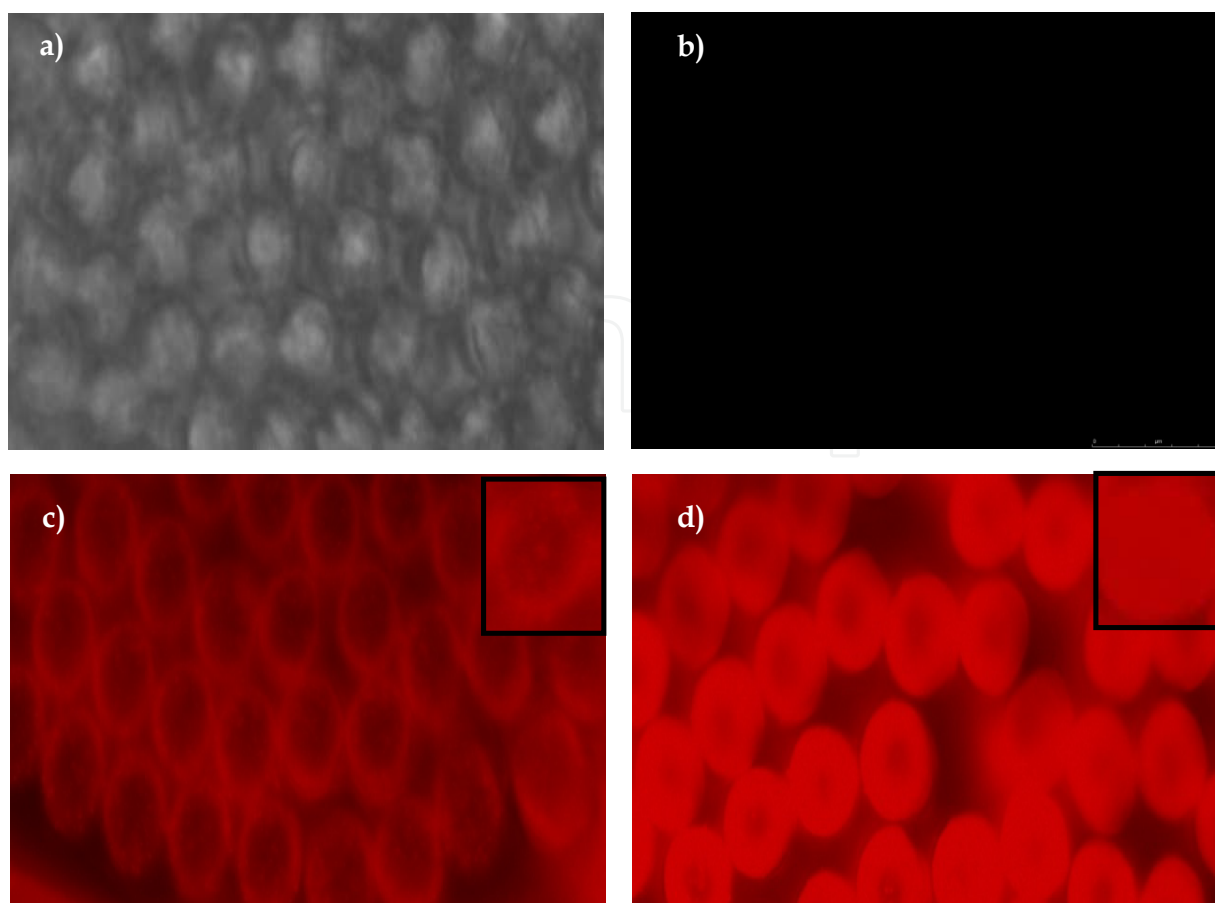


Fig. 16. Fluorescence microscopy (Levafix Red EBA dye): a) polyamide control in bright field b) polyamide control in fluorescence field c) untreated polyamide after dyeing and d) polyamide treated after dyeing.

These results are very promising, because after the plasma treatment the dye is able to penetrate into the fiber so giving high guaranty of good fastness results.

### 3.7 Dyeing process optimization

The dyeing process of polyamide 6.6 is usually performed at boiling temperature and the time required for this process is around 120 minutes (Figure 2a). However, after DBD plasma treatment ( $2400 \text{ W} \cdot \text{min} \cdot \text{m}^{-2}$ ) a new process will be checked with lower temperature and time than those generally used in the polyamide dyeing. This process will start at  $40^\circ\text{C}$ , the temperature is raised until  $70^\circ\text{C}$  with a gradient of  $1^\circ\text{C}/\text{min}$  and remains in this temperature during 60 minutes.

The maximum values of exhaustion for samples with and without treatment (traditional process  $100^\circ\text{C}$ ) and for the samples dyed by optimized dyeing process at  $70^\circ\text{C}$  are shown in table 8.

In this optimized dyeing process, the temperature and dyeing time were reduced of  $30^\circ\text{C}$  and 25% respectively. The best results are obtained when DBD treatment was applied. The reduction of bath exhaustion, when compared the process (b) at  $100^\circ\text{C}$  with process (c) at  $70^\circ\text{C}$  were: 0.5% for the direct dye Sirius 3GDL, 2.6% for the acid dye Telon MGLW, 3.8% for Levafix Red EBA and 4.1% for Red dye Levafix EBA. This way, it is possible to dye polyamide 6.6, treated with DBD, at  $70^\circ\text{C}$  with an excellent bath exhaustion.

Dyes	Exhaustion (%)		
	Without treatment (100°C) - a	With Treatment (100°C) - b	With Treatment Optimized (70°) - c
Direct Orange 3GDL	11.7	97.9	97.4
Acid Telon MGIW	70.0	97.4	94.8
Reactive Remazol Red RB	18.9	92.0	88.2
Reactive Levafix Red EBA	48.1	97.2	93.1

Table 8. Comparison of the maximum exhaustion for different dyeing processes.

The figure 17 shows the bath exhaustion behavior of the reactive dye Levafix Red, for the samples prepared with DBD discharge (b, c) and dyed at 100°C and 70°C respectively, compared with the untreated sample conventionally dyed at 100°C (a). A smoothest curve and excellent bath exhaustion of 93% are observed for the optimized process performed at 70°C.

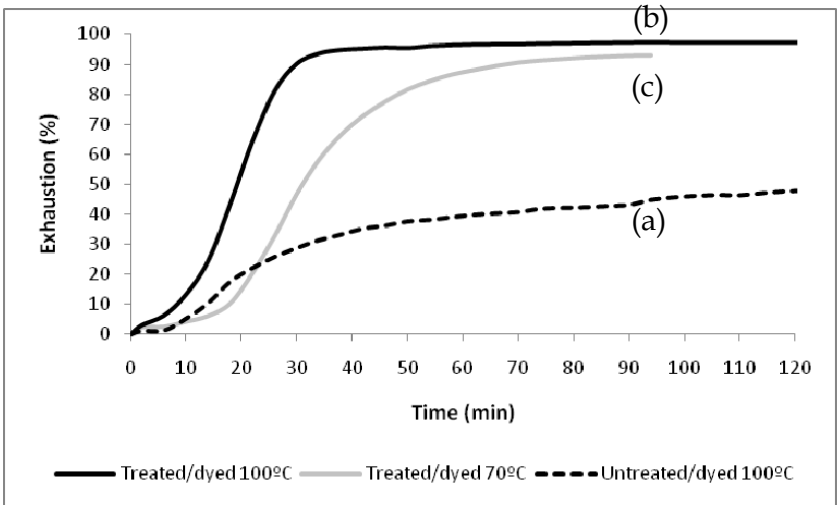


Fig. 17. Exhaustion curves of polyamide dyeing with Levafix Red EBA dye for samples with and without treatment dyed at 100°C (b, a) and with treatment dyed at 70°C (c).

3.7.1 Washing and rubbing fastnesses

Table 9 shows the results of washing fastness for direct, acid and reactive dyes for the optimized dyeing of polyamide 6.6. The results of washing fastness are very good, confirming the level of dye fixation and diffusion into the fiber, despite of this process had been performed at 70°C.

Dyes	Sample	AC	CO	PA	PES	PAC	WO	Color Change
Direct Orange 3GDL	Treated	5	4	5	5	5	4	4
Acid Telon MGIW	Treated	5	4/5	5	5	5	4/5	4/5
Reactive Remazol Red RB	Treated	5	4/5	5	5	5	5	5
Reactive Levafix Red EBA	Treated	5	4/5	5	5	5	5	4

Table 9. Washing fastness of reactive and acid dyeing with previous DBD treatment (norm ISO 105C06/ A1S)

The optimized process performed at lower temperature and time than conventional dyeing of untreated polyamide did not change the washing fastness results. The results of rubbing fastness in dyed fabrics with and without treatment are very good. The value of 4/5 or 5 in the gray scale was obtained for all the samples.

3.8 Cost of DBD plasma treatment

The DBD treatment used the following parameters: power - 1500 W, number of passage - 2, velocity - 2.5 m.min<sup>-1</sup>. The cost to treat one kilogram of polyamide 6.6 fabric (weight : 105 g.m<sup>-2</sup>) is calculated according to table 10.

Dosage (kW.min.m <sup>-2</sup> )	kW.h.m <sup>-2</sup>	Price kW.h (€)	Cost per m <sup>2</sup> (€)	Cost per kg (€)
2.400	0.040	0.094*	0.0038	0.036

Table 10. Cost of DBD plasma treatment (\* mean value of kW.h - Portugal 2010).

Despite the cost of the treatment DBD is around 0.036 €.kg<sup>-1</sup>, several benefits are achieved such as: reduction of 30°C in the temperature of dyeing with an excellent bath exhaustion; reduction of dyeing time of around 25%; reduction of the quantities of dyeing auxiliaries and the possibility to get more intense colors.

4. Conclusion

A relatively low plasma dosage (DBD), around 2400 W.min.m<sup>-2</sup>, can be used to modify the surface of polyamide textile materials, leading to enhanced hydrophilicity and dyeability. Due to these modifications, dyeing of polyamide 6.6 fiber is now possible using nonconventional dyes for this fiber, such as direct and reactive dyes for cotton and wool. The results suggest that the change in exhaustion and dyeing yield in different dyeing conditions closely correspond with the roughness's creation and the changes in chemical oxidative properties induced by DBD treatment in polyamide fabrics. These results reflect directly on dyeing ability of the fiber providing more terminal groups to make dye bonding. The application of anionic dyes in discharged polyamide 6.6 shows extensive improvement of dye exhaustion from baths easily achieving 100% in shorter dyeing times. The kinetics of dyeing in every case is quicker, but leveled results are obtained. It should be noted that deeper dyeing is a great advantage for all anionic dyes since darker shades are obtainable using less amount of dyestuffs. Using plasmatic treatment in polyamide substrates it is possible to obtain decisive energetic gains by dyeing at lower temperatures, to have quite pH independent processes similar to a buffer effect and to reduce dyes and auxiliaries with deeper colors and less pollutant charges. The DBD plasma treatment has an high industrial potential, because it is an environmental friendly dry process. Including a plasma treatment in the processing of the substrate, dyeing properties obtained by using anionic dyes are improved, namely yield, dyebath exhaustion, washing and rubbing fastness, providing a cheap, clean and high quality option for the dyeing of polyamide materials.

Another important possibility is to achieve different and wider gamut of colors in polyamide fibers provided by direct and reactive dyes, with lower energetic and processing time costs and very important environmental gains, meaning excellent opportunities to add value to new textile products.

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